



## Selective photooxidation of alcohols as test reaction for photocatalytic activity

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To Jean-Marie Herrmann, a role model as researcher, friend and excellent human being.

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### ABSTRACT

Twenty-four different titania-based systems synthesized through the sol-gel process varying the precursor (titanium isopropoxide or tetrachloride) and/or the ageing conditions (magnetic stirring, ultrasounds, microwave or reflux) were tested for liquid-phase selective photooxidation of 2-butenol (crotyl alcohol) to 2-butenal (crotonaldehyde) and gas-phase selective photooxidation of 2-propanol to acetone. To the best of our knowledge, the former process is suggested for the first time as test reaction for photocatalytic activity. Interestingly, both test reactions (despite having very different reactant/catalyst ratio and contact times) showed quite similar results in terms of influence of the precursor (titanium isopropoxide leading to better results than titanium tetrachloride) and the metals (the presence of iron, palladium or zinc being detrimental to activity whereas zirconium and especially gold improved the results as compared to pure titania). To our mind, these results give validity to both processes as test reactions for a fast screening of catalysts for photocatalytic transformations. Finally, some gold-containing solids even improved photocatalytic activity of Degussa P25.

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## 1. Introduction

The main application of heterogeneous photocatalysis (at least as far as the number of the publications on the topic is concerned) is the degradation of pollutants present in water through complete mineralization [1–4]. However, the possibility to perform selective photooxidations thus avoiding the use of some typical oxidants such as permanganate or dichromate also seems very attractive in the context of green chemistry. These selective processes are difficult to be carried out in aqueous media though certain selectivity in the adsorption can be achieved making use of the shape-selectivity (zeolites) [5] or the so-called adsorb-and-shuttle concept [6]. In these examples, those chemicals not absorbed on the catalyst are not degraded. Alternatively, photooxidations can be performed in organic media. In this case, the solvent should be resistant enough

to irradiation as not to be degraded, acetonitrile usually being the solvent of choice.

There is no denying the fact that the best test reaction is the target reaction itself, though it is also true that there is a need for relatively simple, fast processes which inform us on the surface properties of a certain solid catalyst. Therefore, for instance, some acid-base reactions (such as dehydration/dehydrogenation of 2-propanol or 2-methyl-3-butyn-2-ol transformation [7–11]) have become “classical” test reaction in heterogeneous catalysis. The study of surface acid-base properties in solids can be also performed using probe molecules such as pyridine (acidity) or carbon dioxide (basicity) [7]. Heterogeneous photocatalysis has also some typical probe molecules (e.g. stearic acid [12–14], methylene blue [13,15] or phenols [16–19]). Furthermore, several selective photooxidation processes (aromatic hydroxylations, hydrocarbon oxidations, alkene epoxidations or alcohol transformations [20–24]) are susceptible to be used as test reactions for photoactivity. Moreover, when different solids are tested as photocatalysts for a certain organic reaction, a reference material

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**Table 1**

Some features concerning characterization of the different titania-based systems used in the present study. For further details, see the references.

Catalyst	UV–vis		XRD		ICP-MS		N <sub>2</sub> isotherms	Reference
	Band gap (eV)	Absorption threshold (nm)	Crystal phases <sup>a</sup> (%)	Crystallite size of anatase (nm)	Nominal content (Metal/Ti %)	Experimental content (Metal/Ti %)	S <sub>BET</sub> (m <sup>2</sup> g <sup>−1</sup> )	
P25	3.19	389	A/R(83:17)	21	–	–	51	[30]
TiO <sub>2</sub> (A)	3.19	389	A/R(97:3)	28	–	–	35	[26]
TiO <sub>2</sub> (A) <sub>r</sub>	3.19	389	A(100)	19	–	–	60	
TiO <sub>2</sub> (A) <sub>m</sub>	3.19	389	A(100)	17	–	–	71	
TiO <sub>2</sub> (A) <sub>u</sub>	3.19	389	A(100)	20	–	–	121	
TiO <sub>2</sub> (B)	2.98	416	A(100)	18	–	–	70	
TiO <sub>2</sub> (B) <sub>r</sub>	2.99	415	A/B(96:4)	17	–	–	83	
TiO <sub>2</sub> (B) <sub>m</sub>	3.09	401	A/B(98:2)	15	–	–	75	
TiO <sub>2</sub> (B) <sub>u</sub>	2.98	416	A(100)	24	–	–	53	
TiO <sub>2</sub> :Pd(A)	3.10	400	A(100)	23	1.0	0.6	65	[25]
TiO <sub>2</sub> :Pd(A) <sub>u</sub>	3.12	397	A(100)	20	1.0	0.6	75	
TiO <sub>2</sub> :Pt(A)	3.15	395	A(100)	31	1.0	0.3	40	
TiO <sub>2</sub> :Pt(A) <sub>u</sub>	3.13	396	A(100)	23	1.0	0.5	57	
TiO <sub>2</sub> :Zr(A)	3.23	384	A(100)	19	1.0	0.8	65	
TiO <sub>2</sub> :Zr(A) <sub>u</sub>	3.22	385	A(100)	21	1.0	0.8	64	
TiO <sub>2</sub> :Fe(A)	3.15	394	A(100)	26	1.0	1.8	48	
TiO <sub>2</sub> :Fe(A) <sub>u</sub>	3.15	394	A(100)	20	1.0	1.7	61	
TiO <sub>2</sub> :Zn(A)	3.17	391	A/R(90:10)	31	1.0	0.7	18	
TiO <sub>2</sub> :Zn(A) <sub>u</sub>	3.24	383	A(100)	19	1.0	0.7	59	
TiO <sub>2</sub> :Ag(A)	3.21	386	A(100)	21	1.0	1.3	53	
TiO <sub>2</sub> :Ag(A) <sub>u</sub>	3.22	385	A(100)	22	1.0	1.7	58	
TiO <sub>2</sub> :Au(15)	3.31	375	A(100)	20	2.0	1.6	59	[28]
TiO <sub>2</sub> :Au(120)	3.30	376	A(100)	20	2.0	1.6	60	
TiO <sub>2</sub> :Au(15) <sub>s</sub>	3.26	380	A(100)	21	2.0	0.3	59	
TiO <sub>2</sub> :Au(120) <sub>s</sub>	3.23	384	A(100)	20	2.0	0.8	58	

<sup>a</sup> Anatase (A), Rutile (R) and Brookite (B).

(typically Degussa P25) is also included in the study for the sake of comparison since, in many cases, non-commercially available reactors are used.

In the present piece of research, 25 different titania-based catalysts are tested for liquid-phase selective photooxidation of 2-butenol (crotyl alcohol) to 2-butenal (crotonaldehyde) and gas-phase selective photooxidation of 2-propanol to acetone and both reactions evaluated as test processes for quick screening of catalysts in photocatalytic transformations. The work starts with a detailed description of the former reaction (crotyl alcohol oxidation) since we have not described it previously. In the latter case (2-propanol transformation) description is less exhaustive as the process is discussed elsewhere [25–27].

## 2. Experimental

### 2.1. Synthesis and characterization of the systems

The syntheses and characterization of the catalysts used in the present work were described in previous papers [25,26,28]. Therefore, different titanium-based systems, either pure or modified with transition metals were synthesized.

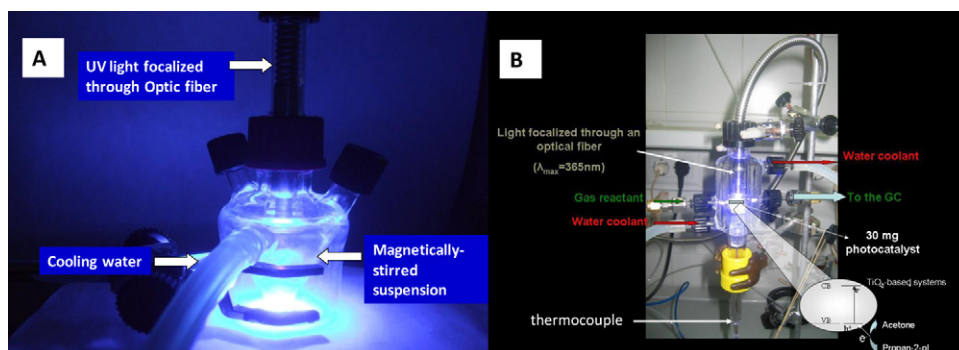
In the case of pure-titania system, they were synthesized through the sol–gel process using titanium isopropoxide or titanium tetrachloride as the titanium precursor. Moreover, the systems were submitted to diverse ageing conditions (magnetic stirring, microwave, ultrasounds or reflux) and subsequently calcined at 500 °C. Nomenclature of pure titania systems includes a letter A or B indicating the precursor used (titanium isopropoxide or titanium tetrachloride, respectively) and a suffix in brackets referring to whether the ageing of the gel was carried out under reflux (R), microwave radiation (M) or ultrasonic irradiation (U). When no suffix was included, it means that the gels

were just submitted to magnetic stirring during the ageing process [26].

As far as metal-containing systems are concerned, different titania-based systems modified with transition metals (Ag, Fe, Pd, Pt, Zn and Zr) were synthesized at a metal/Ti nominal content of 1% by the sol–gel method using titanium tetraisopropoxide as the titanium precursor and both ultrasonic radiation or magnetic stirring as the ageing procedure. Acetylacetonates were used as the metal precursors. Nomenclature includes a suffix referring to the metal, an “A” indicating that the titanium precursor was titanium isopropoxide and when applicable a subscript “u” denoting that the system was aged under ultrasonic radiation (in contrast to conventional magnetic stirring) [25]. Therefore, for instance TiO<sub>2</sub>:Pt(A) and TiO<sub>2</sub>:Pt(A)<sub>u</sub> denote two systems obtained through the sol–gel process from titanium isopropoxide and platinum acetylacetonate ageing under magnetic stirring or ultrasonic irradiation, respectively.

Finally, different gold-containing systems were synthesized through photodeposition of the metal on titania previously obtained through the sol–gel process using titanium tetraisopropoxide as the precursor. Photodeposition was carried out using HAuCl<sub>4</sub> as metal precursor at a 2% nominal content in gold. Nomenclature includes the metal, the deposition time in minutes and a subscript referring to the light intensity (s denotes “soft”, indicating the use of 0.15 W m<sup>−2</sup> instead of 140 W m<sup>−2</sup>). Therefore, for instance, TiO<sub>2</sub>:Au(15)<sub>s</sub> and TiO<sub>2</sub>:Au(15) indicate the systems containing gold photodeposited for 15 min at a light intensity of 0.15 W m<sup>−2</sup> and 140 W m<sup>−2</sup>, respectively. Further details on the catalyst syntheses are given elsewhere [28].

All the systems were characterized using a wide-range of techniques including bulk metal composition (ICP-MS), textural and structural characterization (N<sub>2</sub> adsorption–desorption isotherms, X-ray diffraction, diffuse reflectance UV–Vis etc.). Some of the



**Fig. 1.** Photoreactors used in the present study for liquid-phase selective photooxidation of crotyl alcohol to crotonaldehyde (A) and gas-phase selective photooxidation of 2-propanol to acetone (B).

main features concerning their characterization are summarized in Table 1.

## 2.2. Photocatalytic experiments

### 2.2.1. Liquid phase selective photooxidation of 2-butenol (crotyl alcohol) to 2-butenal (crotonaldehyde)

The experimental device is represented in Fig. 1. Under standard conditions, 3 mL of a stock solution (0.01 M or 0.1 M) of 2-butenol (97% *trans*) in acetonitrile are introduced in the 30 mL double-mouthed heart-shaped reactor. After 7 min bubbling through the solution pure oxygen (6 mL min<sup>-1</sup>), 0.15 mL are sampled, filtered, injected in the GC and taken as initial 2-butenol concentration ( $C_0$ ). The catalyst (typically 20 mg) is then added, the system closed and stirred (1300 rpm) and after 15 min of adsorption in the dark, light is allowed into the reactor. UV light (UV Spotlight source LightningcureTM L8022, Hamamatsu, maximum emission at 365 nm) was focalized on the sample compartment through an optic fiber. Radiant flux in the catalyst compartment was set up at 410, 710 (standard value) or 1050 mW cm<sup>-2</sup> (measured with a Newport UV-meter 818P-015-19 Model). Water used for cooling was thermostated at 10 °C. Reaction profiles were obtained for the same stock solution, each point corresponding to one individual reaction. Once the system had been irradiated for the selected time, the whole suspension was filtered (15 mm diameter, 0.45 μm pore size, Sartorius re. 17559) and analyzed by GC (HP6890 chromatograph equipped with an automatic injector and a HP-PLOTU column (30 m long, 0.53 mm ID, 20 mm film thickness). The main reaction products were crotonaldehyde (*cis* and *trans*), acetaldehyde and CO<sub>2</sub>. This latter species coming from complete mineralization could be followed taking samples from the gas phase of the reactor and injecting them in the GC which was equipped with a Ni methanator (Agilent Part Number G2747A). Moreover, some other very minor species (e.g. carbon monoxide and formaldehyde) were detected as trace levels. Determination of the products was carried out from the corresponding calibration curves.

### 2.2.2. Gas-phase selective photooxidation of 2-propanol to acetone

This experimental device (Fig. 1B) has already been described elsewhere [25] and used the same UV lamp as for experiments in the liquid phase. Therefore, 15 mL min<sup>-1</sup> of O<sub>2</sub> previously bubbled through propan-2-ol at 0 °C was allowed into the photocatalytic reactor, in which 25 mg of catalyst had been placed. The fix bed of the catalyst was in contact with the gas flow. UV light (UV Spotlight source LightningcureTM L8022, Hamamatsu, maximum emission at 365 nm) was focalized on the sample compartment through an

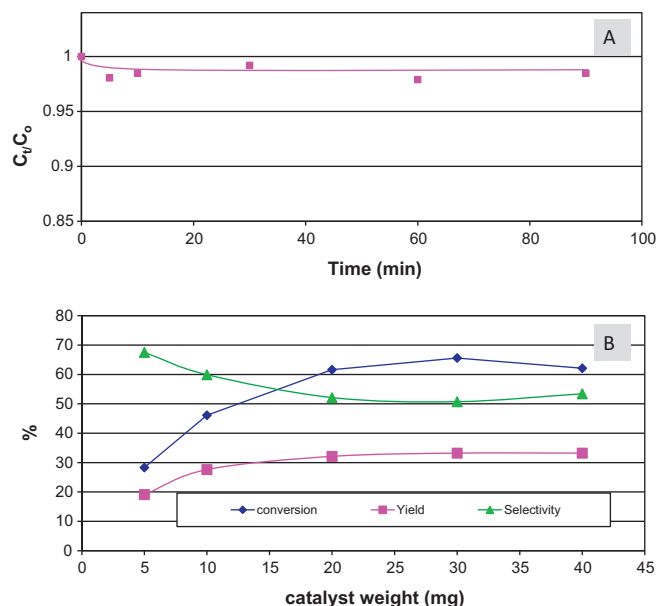
optic fiber. Radiant flux in the catalyst compartment was measured to be 1.1 W cm<sup>-2</sup> (Newport UV-meter 818P-015-19 Model). Reactor was on-line connected to a HP6890 chromatograph equipped with a six-way valve, a HP-PLOTU column (30 m long, 0.53 mm ID, 20 mm film thickness) and a Ni methanator (Agilent Part Number G2747A) which allowed us to determine the percentage of CO<sub>2</sub> resulting from mineralization. Water used for cooling was thermostated at 10 °C.

## 3. Results and discussion

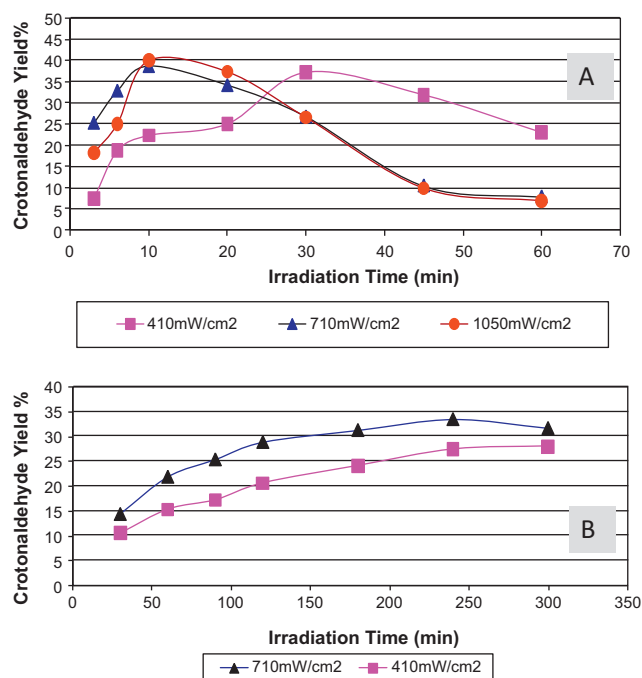
### 3.1. Photooxidation of crotyl alcohol to crotonaldehyde

#### 3.1.1. Blank experiments and adsorption studies

Initially, blank experiments in the dark showed that under standard conditions (20 mg Degussa P25, 3 mL 0.01 M 2-butenol in acetonitrile) crotyl alcohol is not transformed after 90 min. There is only a 2% disappearance which is attributed to adsorption on the catalyst (Fig. 2A). This experiment prompted us to select 15 min as



**Fig. 2.** (A) Adsorption in the dark for 3 mL of a 0.01 M solution of crotyl alcohol in acetonitrile on 20 mg of TiO<sub>2</sub> Degussa P25. (B) Crotyl alcohol conversion and selectivity and yield to crotonaldehyde (%) as a function of the catalyst weight. Conditions: TiO<sub>2</sub> Degussa P25, 710 mW cm<sup>-2</sup>, 3 mL of a 0.01 M solution of crotyl alcohol in acetonitrile and 10 min of irradiation.



**Fig. 3.** Crotonaldehyde yield as a function of time for the irradiation of 3 mL of a 0.01 M (A) or 0.1 M (B) crotyl alcohol solution in acetonitrile at different lamp intensities using 20 mg of TiO<sub>2</sub> Degussa P25 as the catalyst.

the standard time for adsorption before allowing the light into the reactor. Similarly, direct irradiation (710 mW cm<sup>-2</sup>) of the standard solution in the absence of catalyst did not lead to any conversion after 90 min. Therefore, both the photocatalyst and the light seem to be necessary for the reaction.

### 3.1.2. Optimization of other reaction conditions

Optimization of the other conditions was also carried out using TiO<sub>2</sub> Degussa P25 as the catalyst, which is typically utilized as a reference material. Fig. 2B shows the dependence of 2-butenol (crotyl alcohol) conversion and selectivity and yield to crotonaldehyde on the catalyst weight, for an intensity of irradiation of 710 mW cm<sup>-2</sup>. As can be seen, for a weight above 20 mg (the value selected for standard conditions) the yield is quite constant.

The effect of light intensity on the results was then evaluated. Therefore, Fig. 3A shows the evolution of crotonaldehyde yield (standard conditions, C<sub>i</sub> = 0.01 M) as a function of time for 3 different UV light intensities. From that figure it is evident that the profiles obtained for 710 mW cm<sup>-2</sup> and 1050 mW cm<sup>-2</sup> are quite similar whereas that of an irradiation intensity of 410 mW cm<sup>-2</sup> differs. When conversion (not represented) is considered, profiles for 710 mW cm<sup>-2</sup> and 1050 mW cm<sup>-2</sup> are again coincident with a 100% conversion at ca. 25 min whereas reaction is slower at 410 mW cm<sup>-2</sup>. This suggests that at 710 mW cm<sup>-2</sup> the catalyst is already saturated and thus any subsequent increase in intensity does not lead to any improvement in conversion. Therefore, 710 mW cm<sup>-2</sup> was selected as standard radiation intensity. Finally, yields to crotonaldehyde increase with irradiation time up to a conversion of ca. 90% (ca. 10 min for 710 mW cm<sup>-2</sup> and 1050 mW cm<sup>-2</sup> and 30 min for 410 mW cm<sup>-2</sup>). For longer irradiation times, crotonaldehyde yield drops thus suggesting its transformation to other products (as commented below).

Fig. 3B shows a similar profile for C<sub>i</sub> = 0.1 M at irradiation intensities of 410 mW cm<sup>-2</sup> and 710 mW cm<sup>-2</sup>. As can be seen, after 240 min of irradiation ca. 33% yield (at 90% conversion) is achieved at 710 mW cm<sup>-2</sup> whereas the maximum yield for C<sub>i</sub> = 0.01 M with the same lamp intensity was 40% for ca. *t* = 10 min and at 90%

conversion (Fig. 3A). One of the main problems of selective photooxidations is the need for operating at low concentrations in order to obtain significant yields. In this sense, the fact that quite similar yields can be obtained for concentrations differing one order of magnitude is quite interesting and for subsequent experiments C<sub>i</sub> = 0.1 M and light intensity of 710 mW cm<sup>-2</sup> were selected.

Finally, the influence of the presence of water in the reaction medium was studied (Fig. 4). Results obtained in the absence and in the presence of 0.05% water are quite similar whereas for a water content above 0.05%, the yield to crotonaldehyde drops. This is probably due to the competition of water and crotyl alcohol for the adsorption sites since conversion also decreases. Therefore, from there on, before using acetonitrile (Aldrich water content <0.05%) it was desiccated over molecular sieves (Fluka Art. 02573).

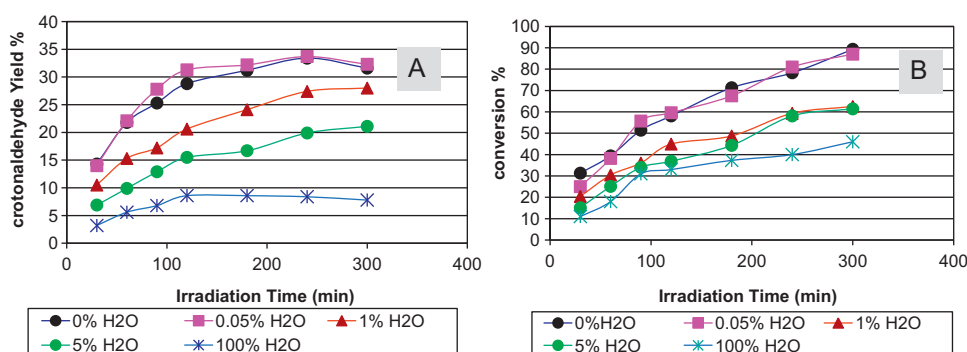
### 3.1.3. Influence of catalyst structure

Once the reaction conditions had been optimized for Degussa P25, different titanium-based systems were tested under similar reaction conditions (0.1 M 2-butenol in acetonitrile, 20 mg catalyst, 710 mW cm<sup>-2</sup> and irradiation times of 30, 90 and 300 min). As commented above, the main features concerning the characterization of these solids are given in Table 1. Moreover, catalytic results for liquid-phase selective photooxidation of crotyl alcohol to crotonaldehyde are summarized in Table 2.

**3.1.3.1. Influence of the titanium precursor and ageing method of the catalyst.** Results obtained for systems consisting of bare-titania aged under different conditions for irradiation times of 30, 90 and 300 min (710 mW cm<sup>-2</sup>) are shown in Table 2 and data for *t* = 300 min represented in Fig. 5A. In general, conversions achieved for similar irradiation times are greater for the solids obtained from titanium isopropoxide as compared to those synthesized from titanium chloride (A and B series, respectively). When the ageing method is considered the solids submitted to reflux (R series) lead to higher conversions. Having a look at the characterization results of those solids (Table 1) the explanation of the improved performance of R solids does not seem easy, though a certain influence of surface area can be found as evidenced by the fact that the reactivity order in B series (B<sub>r</sub> > B<sub>m</sub> > B > B<sub>u</sub>) is the same as that for BET area (83 > 75 > 70 > 53 m<sup>2</sup> g<sup>-1</sup>) and that TiO<sub>2</sub>(A), the solid with the lowest surface area among both A and B series systems, exhibit a particularly low conversion (even lower than that of TiO<sub>2</sub>(B)<sub>r</sub>).

**3.1.3.2. Effect of the presence of transition metals.** Different solids synthesized from titanium isopropoxide and incorporating a metal in the 0.3–1.7 metal/Ti % range, were tested for the reaction. Results for irradiation times of 30, 90 and 300 min are also summarized in Table 2 and data for *t* = 300 min represented in Fig. 5B. For the sake of comparison, those achieved with bare-titania synthesized under similar reaction conditions and reference material Degussa P25 have also been included. Having a look at data in Table 2 it is evident that conversion achieved with all the systems are in a wide range with, for instance, conversions between 8% and 38% for *t* = 30 min or 32% and 95% for *t* = 300 min for the two extreme catalysts (TiO<sub>2</sub>:Fe(A) and TiO<sub>2</sub>:Au(120)<sub>s</sub> respectively). When the influence of the metal is considered, iron, palladium and zinc exhibit lower conversions than the corresponding bare-titania, whereas the presence of silver, zirconium and especially gold is beneficial to photoactivity. For gold-containing systems, the solids obtained for longer irradiation times are more active than those for shorter and the soft conditions are preferable to hard ones, some solids exhibiting even better catalytic performance than Degussa P25. From Fig. 5B one could conclude that some systems (especially gold-containing titania) are more active though less selective. Actually, those solids are so active that the highest conversion levels have been reached at lower irradiation times. In fact, the main





**Fig. 4.** Effect of the presence of water on the conversion of crotyl alcohol (A) and yield to crotonaldehyde (B). Conditions: 20 mg TiO<sub>2</sub> Degussa P25, 710 mW cm<sup>-2</sup>, 3 mL of a 0.1 M solution of crotyl alcohol in acetonitrile.

difference between the tested titanium-containing solids seems to be in the time required to achieve certain conversion level but not in the selectivity itself. In other words, for the same conversion level all the solids tend to exhibit similar crotonaldehyde yields. This is clearly evident in Fig. 6 where both selectivity and yield to crotonaldehyde are represented as a function of conversion. Again, it is clear that irrespective of the catalyst there is a maximum crotonaldehyde yield of ca. 35% achieved at 80–90% conversion. At higher conversions, crotonaldehyde is further oxidized, acetaldehyde and CO<sub>2</sub> being the major products.

#### 3.1.4. *cis/trans* isomerization

As commented above, 2-butenol used in the present study is predominantly in its *trans* form (97%, as determined by GC). However, obtained crotonaldehyde had a *trans* percentage in the 80–90% range. In order to cast further light on the reason for the isomerization, different experiments were carried out. First, a 0.1 M 2-butenol

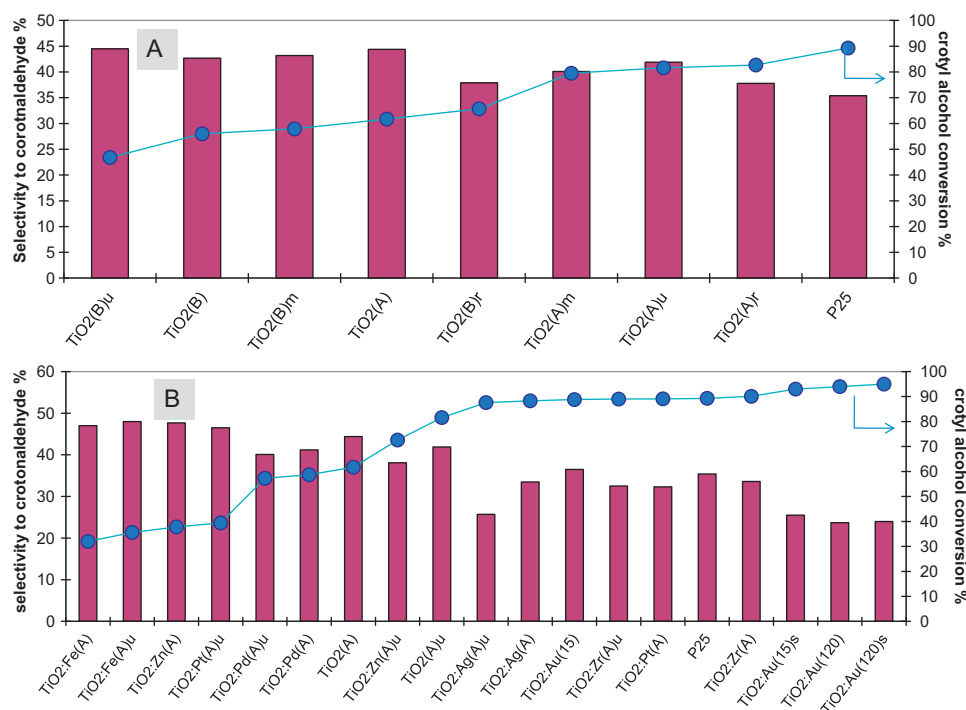
solution in acetonitrile was submitted to UV-light in the absence of catalyst and there was neither isomerization nor transformation into any other product. Similarly, 2-butenol was not transformed on Degussa P25 in the presence of catalyst but in the dark. However, when a 0.1 M 2-butenol (crotonaldehyde, 97% *trans*) solution in acetonitrile was submitted to UV-light (no catalyst) it was partially isomerized (*trans* percentage of 78%) and photooxidized (15% conversion, 14% selectivity to acetaldehyde) after 3 h. When the same crotonaldehyde solution was submitted to light and catalyst (Degussa P25) during the same time (3 h), isomerization was lower (83% of *trans* isomer) and conversion and selectivity to acetaldehyde significantly higher (36% and 34%, respectively).

It is well known that light can lead to *cis/trans* (or *Z/E*) isomerization through the transition of an electron from a  $\pi$  (bonding) to a  $\pi^*$  (antibonding) orbital which leads to the transformation of the C=C to a C–C bond. The single bond already has free rotation which provokes the isomerization, the C=C bond being finally

**Table 2**

Results obtained for liquid-phase selective photooxidation of crotyl alcohol to crotonaldehyde for the different titania-based systems described in the present study in terms of conversion (%) and selectivity to crotonaldehyde and acetaldehyde (%) at different irradiation times. For the sake of comparison, results obtained with Degussa P25 have also been included. Conditions: 20 mg catalyst, 710 mW cm<sup>-2</sup>, 3 mL of a 0.1 M solution of crotyl alcohol in acetonitrile.

Catalyst	30 min			90 min			300 min		
	CONV %	S <sub>CROT</sub> %	S <sub>ACETALD</sub> %	CONV %	S <sub>CROT</sub> %	S <sub>ACETALD</sub> %	CONV %	S <sub>CROT</sub> %	S <sub>ACETALD</sub> %
P25	31	46	13	52	49	16	89	35	12
TiO <sub>2</sub> (A)	14	61	19	31	47	16	62	44	15
TiO <sub>2</sub> (A) <sub>u</sub>	25	51	16	49	48	16	82	42	14
TiO <sub>2</sub> (A) <sub>m</sub>	22	49	16	45	45	16	80	40	14
TiO <sub>2</sub> (A) <sub>r</sub>	23	51	16	51	42	15	83	38	14
TiO <sub>2</sub> (B)	10	74	19	30	46	15	56	43	16
TiO <sub>2</sub> (B) <sub>u</sub>	11	60	15	24	48	15	47	45	16
TiO <sub>2</sub> (B) <sub>m</sub>	31	46	17	46	45	16	58	43	16
TiO <sub>2</sub> (B) <sub>r</sub>	14	65	21	33	44	16	66	38	15
TiO <sub>2</sub> :Pd(A)	10	67	14	22	52	15	59	41	12
TiO <sub>2</sub> :Pd(A) <sub>u</sub>	9	74	15	22	55	14	57	40	12
TiO <sub>2</sub> :Pt(A)	25	52	18	53	44	16	89	32	14
TiO <sub>2</sub> :Pt(A) <sub>u</sub>	9	59	12	12	84	14	39	47	14
TiO <sub>2</sub> :Zr(A)	29	48	16	56	46	17	90	34	14
TiO <sub>2</sub> :Zr(A) <sub>u</sub>	25	52	18	53	43	16	89	33	13
TiO <sub>2</sub> :Fe(A)	8	61	16	16	47	16	32	47	18
TiO <sub>2</sub> :Fe(A) <sub>u</sub>	9	60	15	18	52	17	36	48	17
TiO <sub>2</sub> :Zn(A)	8	54	16	14	48	20	38	48	16
TiO <sub>2</sub> :Zn(A) <sub>u</sub>	20	43	15	37	48	15	73	38	13
TiO <sub>2</sub> :Ag(A)	27	54	14	50	50	14	88	34	11
TiO <sub>2</sub> :Ag(A) <sub>u</sub>	25	60	14	55	44	14	88	26	12
TiO <sub>2</sub> :Au(15)	35	49	16	62	44	16	89	37	13
TiO <sub>2</sub> :Au(120)	37	44	16	61	39	16	94	24	10
TiO <sub>2</sub> :Au(15) <sub>s</sub>	37	46	15	69	39	12	93	26	9
TiO <sub>2</sub> :Au(120) <sub>s</sub>	38	46	15	70	39	13	95	24	8



**Fig. 5.** Results obtained for liquid-phase selective photooxidation of crotyl alcohol to crotonaldehyde for the different bare-titania (A) or metal-containing systems (B) described in the present study in terms of conversion (%) and selectivity to crotonaldehyde (%) after 5 h of irradiation. For the sake of comparison, results obtained with Degussa P25 have also been included. Conditions: 20 mg catalyst, 710 mW cm<sup>-2</sup>, 3 mL of a 0.1 M solution of crotyl alcohol in acetonitrile. Catalysts are ranked in terms of increasing final conversion from left to right.

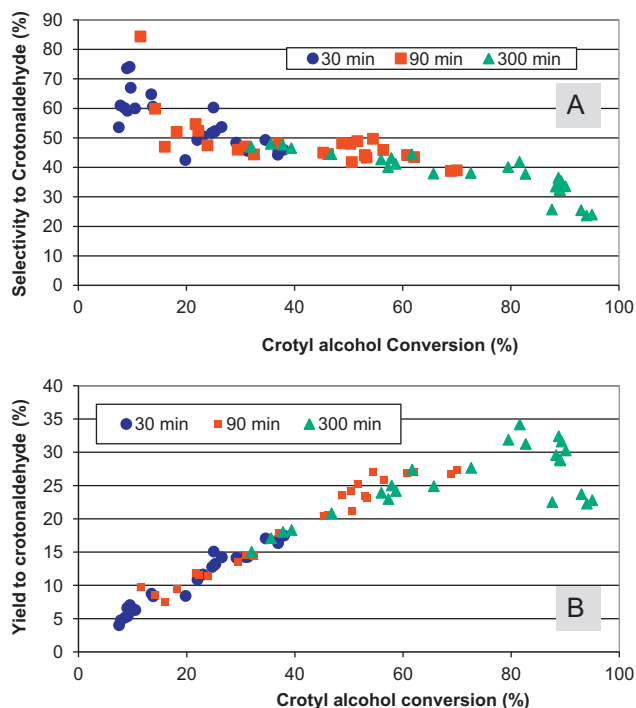
recovered. For an isolated C=C bond,  $\pi \rightarrow \pi^*$  transition has a  $\lambda_{\max}$  of ca. 180 nm. The UV lamp used in the present study has a  $\lambda_{\max}$  of 365 nm (100% intensity) though some other emission lines are present at lower wavelengths. It is possible that for 2-butenol the

spectral lines of the lamp are not energetic enough as to provoke the  $\pi \rightarrow \pi^*$  transition whereas in crotonaldehyde the conjugation of C=C to a C=O bond reduces the difference between  $\pi$  and  $\pi^*$  levels to energy values provided by the lamp thus resulting in crotonaldehyde partial isomerization.

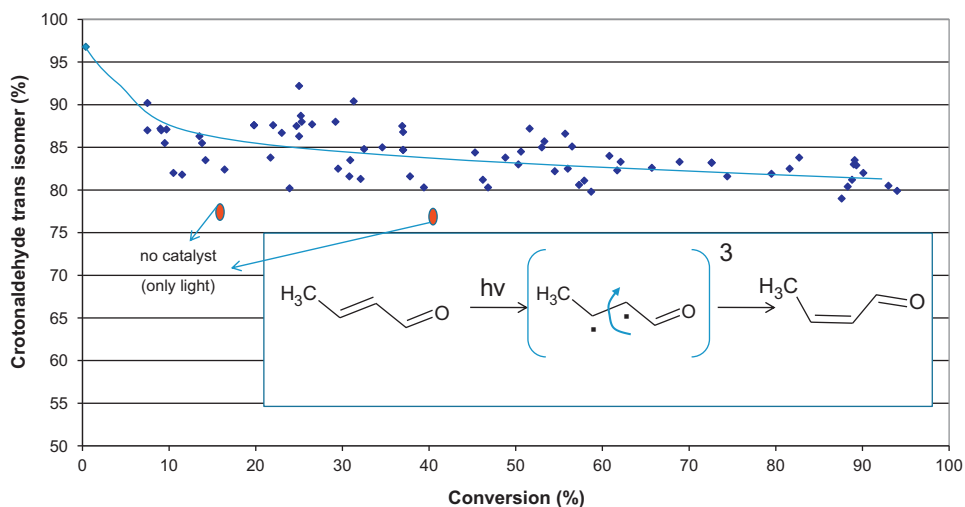
McGreer and Page [29] determined that on irradiation ( $\lambda = 300$  nm) at room temperature of a *trans*-crotonaldehyde solution equilibrium was reached when *trans* and *cis* isomers were present in the ratio of 79:21. Moreover, according to the authors, the *trans*-isomer in conjugated forms have a marked stability due to the high resonance stabilization of this form, whereas the stability of the *cis*-form is reduced by distortion from planarity of the carbonyl group of the conjugated system. In our case, assuming that our crotonaldehyde solution in acetonitrile behaved as pure crotonaldehyde, the observed *trans/cis* ratio on irradiation (78:22) suggest that equilibrium had not been reached yet whereas the higher conversion levels achieved with the catalyst confirm that the process is photocatalytic. Furthermore, when all the systems were tested for crotyl alcohol transformation into crotonaldehyde, obtained results (Fig. 7) show a certain decrease in the *trans* isomer with conversion, though the percentage of *trans* isomer do not reach the value obtained for direct photoisomerization (without catalyst). This could confirm that photooxidation of crotonaldehyde proceeds exclusively or in an easier way through the less stable *cis*-form. In any case, these results require further studies, in particular competitive reactions (from mixtures of *cis*- and *trans*-crotonaldehyde).

### 3.2. Photooxidation of 2-propanol to acetone

All the titanium-based systems were also tested for gas-phase selective photooxidation of 2-propanol. In this case, optimization of reaction conditions and mechanistic discussions were already described in previous studies [25–27]. Therefore, we will focus now on the catalytic results for the 25 different



**Fig. 6.** Dependence of selectivity (A) and crotonaldehyde yield (B) on crotyl alcohol conversion. Data correspond to suspensions containing 20 mg of the different catalysts in 3 mL of a 0.1 M solution of crotyl alcohol in acetonitrile irradiated at 710 mW cm<sup>-2</sup> for 30, 90 or 300 min.



**Fig. 7.** Dependence of the percentage of *trans* crotonaldehyde on crotyl alcohol conversion. Data correspond to suspensions containing 20 mg of the different catalysts in 3 mL of a 0.1 M solution of crotyl alcohol (97% *trans*) in acetonitrile irradiated at  $710 \text{ mW cm}^{-2}$  for 30, 90 or 300 min. Results obtained for irradiation of the solution in the absence of catalyst for 3 h or 7 h have also been included. The inset describes the *trans/cis* isomerization.

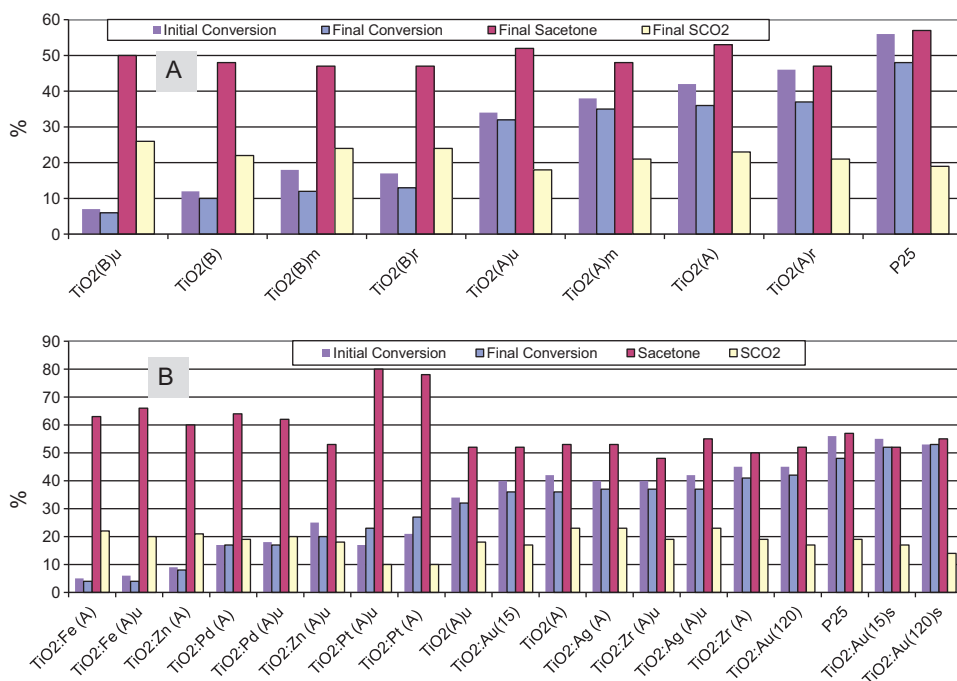
titania-based systems used in the present study. The main results in terms of initial conversion and final conversion, selectivity to acetone and  $\text{CO}_2$  for a time-on-stream of 5 h are going to be commented.

### 3.2.1. Influence of catalyst structure

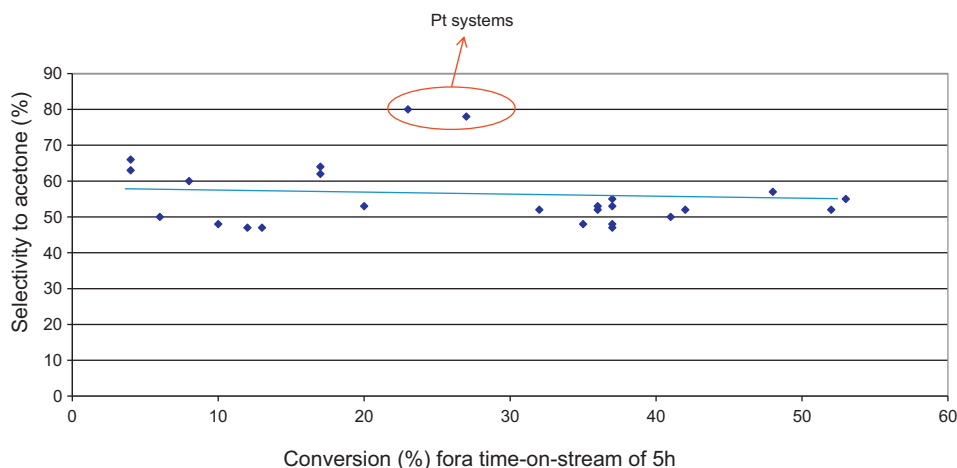
**3.2.1.1. Influence of the titanium precursor and ageing method of the catalyst.** Results obtained for bare-titania are represented in Fig. 8A. In a similar way as for liquid-phase oxidation of crotyl alcohol, the solids belonging to A series (titanium tetraisopropoxide as the precursor) exhibit better catalytic performance as compared to those from B series (titanium tetrachloride). Furthermore, when the ageing method is considered, the highest conversions within

a series are obtained with solids aged under reflux whereas the lowest values are achieved for systems treated under ultrasounds.

**3.2.1.2. Effect of the presence of transition metals.** The main results obtained for gas-phase selective photooxidation of 2-propanol to acetone on metal-containing systems are represented in Fig. 8B. Again, catalytic behavior reminds that of the solids in the liquid-phase photooxidation of crotyl alcohol. Indeed, the trends are even more clearly marked, especially in the case of platinum. Therefore, if results for  $\text{TiO}_2(\text{A})$  and  $\text{TiO}_2(\text{A})_{\text{u}}$  are taken as the reference, the incorporation of iron, zinc, palladium or platinum is detrimental to the activity, whereas the opposite holds true for the addition of silver, zirconium and especially gold, whose photoactivity is higher in some cases than that of Degussa P25. Results



**Fig. 8.** Results obtained for gas-phase selective photooxidation of 2-propanol on different bare-titania (A) or metal-containing systems (B) described in the present study in terms of initial conversion (%) and molar conversion (%), selectivity to acetone (%) and selectivity to  $\text{CO}_2$  (%) for a time-on-stream of 5 h. For the sake of comparison, results obtained with Degussa P25 have also been included. Catalysts are ranked in terms of increasing final conversion from left to right.



**Fig. 9.** Dependence of selectivity to acetone on 2-propanol conversion for all the titania-based systems used in the present study. Highlighted values correspond to platinum-containing titania.

obtained for bare and metal-containing titania in crotyl alcohol and 2-propanol transformations are interesting since the same or similar activity order for the tested solids are obtained for two reactions performed in the liquid or the gas phase, respectively, despite the fact that the reactant/catalyst ratio and contact times are much lower in the latter case. This gives validity to both processes as test reactions for a fast screening of catalysts for photocatalytic oxidation of alcohols thus avoiding carrying out a more in-depth characterization of the solids if the activity is null.

When selectivity is plotted as a function of conversion for all the solids (Fig. 9), it is quite constant, the only two values significantly differing from the general trend being those achieved on platinum-containing solids. In fact, in a previous study [26] a more-in depth study of photocatalytic activity of  $\text{TiO}_2\text{:Pt(A)}_x$  was carried out and the effect of the different oxidation/reduction pre-treatments on its photocatalytic performance for selective oxidation of 2-propanol to acetone was discussed. Results showed that the system was quite interesting, exhibiting some strong-metal-support interaction (SMSI) under certain circumstances which was particularly beneficial for selectivity to acetone. This would suggest that gas-phase selective photooxidation of 2-propanol to acetone is more “sensitive” than crotyl alcohol transformation to these SMSI effects, though this requires further studies. Other photocatalytic systems based on semiconductors different to titania are currently being studied in order to check if the above-described test reactions are sensitive to the semiconductor itself and, for instance, the selectivity to crotonaldehyde vs. crotyl alcohol conversion profile is different depending on the semiconductor which would be also very interesting.

#### 4. Conclusions

Twenty-five different solids consisting in titania-based systems synthesized through the sol–gel process (either alone or modified with metals) and reference material Degussa P25 were tested for liquid-phase selective photooxidation of crotyl alcohol to crotonaldehyde and gas-phase selective photooxidation of 2-propanol to acetone. Results obtained for both processes showed some similar trends. Therefore, regarding bare-titania, in general, the solids obtained for titanium tetraisopropoxide (A series) were more active than those synthesized from titanium tetrachloride (B series), the most and the least active systems being  $\text{TiO}_2\text{-(A)}_f$  (ageing of the gel under reflux) and  $\text{TiO}_2\text{-(B)}_u$  (ageing under ultrasounds), respectively. In any case, activity levels achieved for bare-titania

were lower than those of Degussa P25, a reference material in photocatalysis. When metal-containing solids are considered, the incorporation of iron, palladium or zinc is detrimental to activity whereas zirconium and especially gold lead to better results as compared to pure titania, some gold-containing systems exhibiting better activity than Degussa P25. It seems that photodeposition of gold at low lamp intensities is better than the use of higher values. In the case of crotyl alcohol transformation, the diverse catalysts differ on the time required to achieve a certain conversion level but for the same conversion values all systems exhibit similar selectivities to crotonaldehyde. Interestingly, as the oxidation of crotyl alcohol to crotonaldehyde proceeds there is a *trans/cis* isomerization which is apparently slower in the presence of the photocatalyst. This suggests the preferential photooxidation of crotonaldehyde through its *cis* form.

For 2-propanol transformation into acetone, selectivities achieved with all the systems are quite similar and quite constant with conversion, the only exception being platinum-containing solids which showed quite high selectivity values to acetone (in the 78–80% range at 22–28% conversion). This seems to suggest that this test reaction is more sensitive to the presence of the metal. All in all, these results suggest that both test reactions can be used for fast screening of photocatalytic activities especially for solids synthesized under quite similar reaction conditions.

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